7 ENVIRONMENTAL MANAGEMENT PROGRAMS

7.1 OVERVIEW

Catherine S. Klusek

In its Five-Year Plan, the DOE Office of Environmental Management (EM) specifies that policies be instituted to establish, assess and maintain high quality analytical laboratories to provide the quality data needed to fulfill the needs and requirements for the operation of restoration and waste management at DOE sites. The Office of Compliance and Site Coordination, through its Analytical Services Division (EM-26), has designed and is implementing an Analytical Services Program (ASP) to address these issues. Under the direction of EM-26, EML is currently involved in three components of the Quality Assurance (QA) Program elements of the ASP: the QA guidance and supporting documents, the Performance Evaluation Programs, and the Assessment Program. The objective of the QA element of the ASP is to develop, integrate and implement a comprehensive QA program that addresses the full scope of a laboratory's performance from sampling through analysis to data evaluation.

In addition to EML's core effort in EM-26's QA programs described above, other projects are undertaken on a fiscal year basis depending on the needs of headquarters and staff availability. These activities are of two types: (1) direct support to EM-26 in addressing issues relevant to DOE's environmental needs and planning efforts through participation in working groups, presentations and technical reviews, and (2) technical activities to continually improve the analytical capability of EML and DOE support contractors and to introduce improvements or additional samples/analytes to the ongoing performance evaluation programs. During 1995 several areas of analytical development utilizing liquid scintillation techniques were pursued.

Additional projects are reported which support other offices in EM. Support for the Office of Technology Development (EM-50) continued through the efforts of EML's Technical Program Manager (TPM).

EM-26 QA Program Support

7.2 EM-26 QA DOCUMENTS

Michael Johnson, Catherine S. Klusek, Vivian Pan and Hemant Pandya

As part of an ongoing effort in QA guidance, performance objectives and criteria for QA assessments continue to be developed. In 1995, EML presented a draft plan for assessing sampling activities, including the key elements necessary for effective programmatic control of sampling services, at the Eleventh Annual Waste Testing and Quality Assurance Symposium, American Chemical Society, in Washington, D.C.

EM-26 has developed a comprehensive assessment program for the technical and QA management activities of EM's environmental sampling and analysis facilities, external laboratories and field operations to ensure that data collection operations comply with DOE QA requirements and laboratory-specific QA/QC requirements and that sampling and analysis plans are being effectively implemented. A course document was developed and has now been published (Johnson, et. al., 1995) to address concepts of the EM-26 Assessment Protocol and to complement concepts introduced in the EM-20 Auditor/Lead Auditor Training Course at DOE Headquarters. The course was designed as a three-day tutorial covering all aspects of a technical and management assessment. The training material covered areas of EM organization and QA requirements, concepts and philosophy of assessment, the EM-26 assessment program and related protocols, and the techniques of conducting assessment interviews. The course focused mainly on the training of technical specialists for assessments using established DOE Guidance Documents DOE/0158P and DOE/0159P. Potential QA management team members were trained with established Performance Objectives and Criteria in Management Assessment Guidance Document DOE/EM-0161P.

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Report DOE/EM-0159P, May (1994)
U.SDOE, EM Analytical Services Division

"Quality Assurance Guidance for Management Assessment in Support of EM Environmental Sampling and Analysis Activities"
Report DOE/EM-0161P, May (1994)

7.3 QUALITY ASSESSMENT PROGRAM (QAP)

Colin G. Sanderson, Catherine S. Klusek, Pamela Greenlaw,
Isabel M. Fisenne, Vivian Pan, Anna Berne, Steven Minick, Pamela Perry,
William Rivera, Salvatore C. Scarpitta, Marie Lawrence, and Richard Godwin

The EML Quality Assessment Program (QAP) is designed to test the quality of the environmental measurements reported by contractor laboratories to the DOE's Office of Environmental Management (EM) and the Office of Environment, Safety and Health (EH). Under QAP, real or synthetic environmental samples that have been prepared and thoroughly analyzed at EML for as many as 20 radionuclides are distributed semi-annually to the contractors and other participating laboratories. Each participant receives five samples consisting of blended contaminated soil and vegetation, and air filters and water samples spiked with radionuclides. Most of the soil and vegetation samples have been collected from locations where the radioactive concentrations in these matrices are known to be higher than average background values.

During 1995, QAP samples were distributed on March 1 (QAP-42) and on September 1 (QAP-43). Two EML reports were issued: EML-565 (Sanderson, Pan and Greenlaw, 1995) covered the participants' results for the QAP-41 sample distribution; EML-569 (Sanderson, Greenlaw and Pan, 1995) covered the participants' results for the QAP-42 sample distribution.

During this past year, 127 laboratories received QAP samples. This was a decrease of 2 over 1994 but an increase of 18 over 1993 and an increase of 35 over 1992. One hundred and five (105) laboratories reported data for the QAP-41 sample distributions and 111 reported data for QAP-42.

The total number of analyses performed by all participants in 1995 (QAP-41 and QAP-42) was 5935, about 27% more than was reported in 1994. In general, the 1995 data reported, while satisfactory, was not as good as in 1994. For 1995, 68% of the reported results were within 20% of the EML value; 10% differed from the EML value by more than 50%. In 1994, about 75% of the reported results were within 20% of the EML value, and 8% of the results differed from the EML value by more than 50%.

Acknowledgment -- The following support personnel contributed to the success of this program: Sylvia Hulse, Andrea Delgado, Kevin J. Clancy, Arnold Boyd, William Jackson, Camille Marinetti, Herbert W. Feely, Matthew Williamson, Brenda O. Jones and Nancy Chieco

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7.4 GAMMA SPECTROMETRY DATA VALIDATION PROGRAM

Karin M. Decker and Colin G. Sanderson

The annual gamma spectrometry data validation program will measure the ability of various DOE laboratories to use commercially available software and in-house programs to accurately identify and quantify the nuclides in a complex spectrum. Previous work (Sanderson, 1988; Decker and Sanderson, 1992) indicated that most programs did a good job of detecting and resolving peaks when used properly, but work was needed to improve the algorithms that convert gamma-rays to nuclide concentration. The goal of this program is to assess the capability of DOE laboratories and DOE contractors to perform routine gamma spectra analysis required for EM projects, site evaluations and other DOE programs. Synthetic spectra were created using a computer code developed at the Pacific Northwest National Laboratory and converted into a variety of formats which could be read by most PC based systems. It was found that many laboratories were using stand-alone Canberra Microvax based systems which use magnetic tape for data input. The synthetic spectra were converted to this format and put on tape with help from Canberra and sent out to be tested. The spectra will now be sent out to laboratories performing EM analyses. Participants will be asked to report nuclide identities, concentrations and uncertainties, as well as Minimum Detectable Levels (MDL). The nuclear data reference used and method of calculating MDL will also be requested in order to determine possible sources of discrepancy. The laboratories will submit their results to EML for assessment and publication.

References

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Applied Radiation and Isotopes, 43, 323-337 (1992)

7.5 TECHNICAL ASSISTANCE PROGRAM

Vivian Pan

The QAP participating laboratories' analytical results can be produced by different analytical methods and procedures. The DOE QAP, described in Summary No. 7.3, is a performance driven intercomparison program. That is, DOE focuses on the quality of the end analytical results independent of the analytical method rather than on results which are from prescribed analytical methods. As part of the customer support for QAP, EML provides technical assistance for participating laboratories with poor or inconsistent results. In 1995, EML conducted a technical evaluation of the Fernald Environmental Restoration Management Corporation Analytical Laboratory Services uranium analytical system in response to inconsistent performance in recent QAP evaluations. Data and document reviews were carried out to determine whether Standard Operating Procedures (SOPs) were technically accurate and appropriate for the samples and if the analytical system was biased. The evaluation concluded that the method in use was not sensitive enough for quantitative analyses at environmental levels. The agreed upon changes to the analytical method have resulted in subsequent data results with "acceptable" evaluations.

7.6 DOE MIXED ANALYTE PERFORMANCE EVALUATION PROGRAM (MAPEP)

Catherine S. Klusek, Colin G. Sanderson, Isabel M. Fisenne, Pamela Greenlaw, Anna Berne, Pamela Perry, William Rivera, Michael Johnson, William C. Rosa, Ada Kong and Yulin L.Tan

The DOE's Mixed Analyte Performance Evaluation Program (MAPEP) is administered by DOE's Radiological and Environmental Science Laboratory (RESL), ID. The program evaluates DOE contractor performance in analyzing typical radionuclide, inorganic and organic analytes found in mixed waste samples at the DOE complex cleanup sites. MAPEP was mandated by a policy directive from the Assistant Secretary for EM in 1994. EML is participating in MAPEP as a first tier laboratory, three in total, which evaluate, test and certify the mixed analyte samples for distribution.

MAPEP will distribute samples twice a year, in June and December. Initially, the samples will alternate between a water and a solid sample. The first implementation round of MAPEP was in January 1995. The sample (MAPEP-94-W2) was a mixed radiological and inorganic water sample. EML completed the verification round analysis in August 1994. The samples were analyzed for 5 radionuclides (^{137}Cs, ^{57}Co, ^{60}Co, ^{90}Sr and $^{239.240}$Pu) and 11 priority inorganic pollutants. The results

of the reference laboratories were reported in Dahlgran (1995).

During 1995, EML completed the verification rounds for MAPEP-95-S2 and MAPEP-95-W3. The MAPEP-95-S2 sample was a soil containing radionuclide and inorganic constituents. The sample was analyzed for 6 radionuclides (^{137}Cs, ^{60}Co, ^{90}Sr, ^{238}Pu, ^{239,240}Pu and ^{241}Am) and 18 inorganic elements (Al, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Th, V and Zn). Inorganic data was generated using traditional atomic absorption techniques. The MAPEP-95-W3 water samples was also a mixture of radionuclides and inorganic constituents. The samples were analyzed for 10 radionuclides (^{54}Mn, ^{57}Co, ^{90}Sr, ^{137}Cs, ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{234}U, ^{235}U,and ^{238}U) and 6 RCRA elements (As, Ba, Cd, Cr, Pb and Se). Inorganic data was generated using traditional atomic absorption techniques and state-of-the-art Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).

Preparations are in progress to provide support to MAPEP-96-S3 for the verification of semi-volatile organic analytes (pesticides) as well as radiological and inorganic components. A project plan has been developed to demonstrate proficiency in the testing of volatile organic constituents utilizing standard US EPA methods and measurement techniques.

References

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"Work Plan for Mixed-Analyte Performance Evaluation Soil Sample MAPEP-95-S2"
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7.7 EXTRACTION EFFICIENCIES OF Ra, U, Th, Pu, Am,Cm AND Np IN THREE COMMERCIALLY AVAILABLE EXTRACTIVE SCINTILLATORS USING PERALS™ SPECTROMETRY

Salvatore C. Scarpitta

The extraction efficiencies (EEs) of ^{210}Pb, ^{226}Ra, ^{232}U, ^{230}Th, ^{244}Cm, ^{242}Pu, ^{243}Am and ^{237}Np into three commercially available liquid extractive scintillators have been measured under various chemical conditions. A subject paper was presented at the 41st Annual Bioassay, Analytical and Radiochemistry Conference in Boston, MA, in November 1995. The extractive scintillators were either aliphatic amine sulfates (URAEX^{R} and THOREX^{R}) or a phosphoric acid /nitrate derivative

(ALPHAEX^{R}). One to two milliliter aliquots of these toluene based extractive scintillators, intended for measurement in a PERALS^{TM} alpha counting system, can be mixed into a Liquid Scintillation (LS) cocktail and measured by conventional LS counting. The PERALS system rejects unwanted ß or γ signals. Using ^{232}U as a tracer, sulfuric, nitric and hydrochloric acids were tested over a range of normalities to determine their effect on the EE. The optimum EEs for URAEX and THOREX were from dilute sulfuric acid, whereas that of ALPHAEX was from nitric acid. The effect of aqueous phase pH on the EEs for each nuclide was also tested at the optimum salt (SO_4 or NO_4) and acid conditions of each extractant. Each extractive scintillator has the capability of extracting either one or several actinide elements, depending on the pH, acid normality or salt concentration of the aqueous phase. If an aqueous sample contains several alpha emitting actinides, then additional separation chemistry steps may not be required before final measurement, depending on (1) the choice of extractant, (2) chemical conditions during extraction, and (3) the alpha energy difference between co-extracting interferants and the nuclide of interest. The final choice of a yield tracer for a specific radioanalytical application would also be determined by the energy resolution of the PERALS^{TM} Spectrometer, typically 0.250 MeV.

7.8 CALIBRATION OF A LIQUID SCINTILLATION COUNTER FOR α, ß AND CERENKOV COUNTING

Salvatore C. Scarpitta and Isabel M. Fisenne

Liquid scintillation (LS) counting systems are designed to detect low-energy (e.g., ^{3}H, ^{14}C) to high energy ß particles (i.e., ^{90}Y, ^{106}Rh), and α particles. Samples containing mixtures of radionuclides that emit α or ß particles or conversion electrons can be detected and quantified using variations on the LS counting technique. Depending on the LS cocktail (scintillator-solvent mixture), the alpha detection efficiency is generally >95%, whereas the beta detection efficiency is dependent on energy, spectral shape and cocktail. Typically, ß particles with maximum energies (E_{max}) >0.250 MeV are detected with >90% counting efficiency.

One variation on the LS counting technique is Cerenkov counting, an adjunct to LS counting, that does **not** require a LS cocktail (Scarpitta and Fisenne, in press). Cerenkov counting may prove effective in a rapid analysis scheme for specific radionuclides (i.e., ^{210}Pb); it may provide an additional or verification methodology in the calibration of reference radionuclide solutions; and it may reduce the hazardous waste stream from the analytical operations. Cerenkov counting in aqueous samples is applicable to ß particles with endpoint energies >0.263 MeV. The Cerenkov counting efficiency is typically 40% per MeV or ß particles with endpoint energies above the Cerenkov threshold. Alpha particles are not detected in pure aqueous solutions unless an additive is used to enhance the detection counting efficiency.

Calibration data are compiled for 25 radionuclides that were individually measured in a Packard Tri-Carb 2250CA LS Analyzer (Packard Instrument Co., Downers Grove, IL) by both conventional and Cerenkov detection techniques. The relationships and regression data between the quench indicating parameters and the LS counting efficiencies were determined using microliter

amounts of tracer added to low ^{40}K borosilicate glass vials containing 15 mL of Insta-Gel XF (Packard Instrument Co., Downers Grove, IL) scintillation cocktail. Cerenkov data were obtained using various ß emitters measured in plastic vials containing a wavelength shifter solution.

In general, about 50% of the instrument background was in the 0-50 keV energy region. The average instrument background, using 20 mL plastic vials containing 10 mL of ultra-pure water, was 0.255 $\pm$ 0.018 counts per second (cps) for a 0-50 keV region of interest (ROI). The average background count rate for glass vials (0.346 $\pm$ 0.010 cps) was about 30% higher than the plastic vials. Based on replicate background measurements, the lower limit of detection (LLD) for a one-hour count at the 95% confidence level, using water as a solvent, was 0.024 cps and 0.028 cps for plastic and glass vials, respectively. The LLD for a one-hour count, using 10 mL of a waveshifter solution, was 0.039 cps for plastic vials. The LLD, expressed as activity, ranged from 46 to 56 mBq (2.8 - 3.4 dpm) for conventional LS counting. This assumes (1) a 100% counting efficiency, (2) a 50% yield of the nuclide of interest, (3) a 1 h measurement time using low background plastic vials, and (4) a 0-50 keV ROI. The LLD may be reduced an order of magnitude if the yield recovery exceeds 90% and a lower background region (i.e., 100 - 500 keV alpha ROI) is used.

Detection efficiencies were linear over a 3 orders of magnitude range in ß activity (10 - 10,000 mBq) for both LS and Cerenkov counting. A linear relationship was observed for the Cerenkov counting efficiency (CCE) as ß energy increased from 0.300 to 2 MeV, whereas the LS efficiency was >90% for ßs with energy in excess of 0.250 MeV. A comparison of the data showed that the CCE was 20-50% less than the LS counting efficiency for ß particles with maximum energies in excess of 1 MeV.

Reference

Scarpitta, S. and I. M. Fisenne,
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Int. J. Appl. Rad. Isotopes, in press

Other EM Projects

7.9 COMPUTING TOTAL UNCERTAINTIES IN RADIOCHEMICAL ANALYSES

Anna Berne

When an environmental sample is analyzed for some radioactive element using radiochemical methods, the uncertainty of the calculated result has to be reported so that appropriate assessment can be made. Often, only one aliquot of the sample is taken and a single determination is made. Under those circumstances, the total uncertainty is calculated using the "propagation of errors" approach, which takes into account the uncertainties associated with the analytical procedures, as well as the counting error(s) contributed by the counting step of the method. However, there is no agreement in the radioanalytical community as to the exact equations to use. As part of a project supported by

EM-40, a systematic process has been developed to compute uncertainties in the constituent components of the analytical procedure as well as the Total Propagated Uncertainty (TPU). This was reported at the 41st Annual Bioassay, Analytical and Radiochemistry Conference in Boston, MA, in November 1995. The equations for computation have also been incorporated into a code for use in the spreadsheet application, QuattroPro™. Using the spreadsheet with appropriate inputs permitted an analysis of variations in the TPU as a function of several different variables. The relative importance of the "counting error" can be ascertained. A handbook for calculating TPUs is being prepared.

7.10 TECHNICAL PROGRAM MANAGER (TPM) ACTIVITIES FOR THE OFFICE OF TECHNOLOGY DEVELOPMENT (EM-50)

Karen A. Stevenson

The DOE's Office of Technology Development (EM-50) has been given the mission to direct an aggressive national campaign to accelerate the development of innovative technologies to remediate contaminated DOE sites. The responsibility of the Technical Program Manager (TPM) under this initiative is to be the site single point of contact for headquarters oversight.

During this past year, Karen Stevenson (TPM) again served as a technical focus group committee member for the selection of Technical Task Plans (TTP) and review of already funded programs under the Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP) under the EM Focus Area initiative. The meeting was held in Denver, CO, May 9-10, 1995. Principal investigators of ongoing programs gave oral progress reports to the reviewers.